Improvements in or relating to process of pickling iron and its alloy

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Inventor:
Applicant: PAUL DE LATTRE
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Abstract of **GB517998**

517,998. Pickling metals. LATTRE, P. DE. Aug. 20, 1938, Nos. 24581 and 24582. Convention dates, Aug. 21, 1937 and Aug. 6, 1938. [Class 82 (ii)] Iron and its alloys are pickled by means of a sulphuric acid solution to which are added hydrochloric acid and a limiter, the porportions of the reagents being such as to cause the formation of ferrous chloride at the expense of ferrous sulphate. The pickling solution is regenerated by simultaneous additions of the two acids and the limiter in such amounts as to maintain substantially constant the concentrations of these three constituents and to keep up the partial conversion of ferrous sulphate into ferrous chloride. Used-up pickling solution may be rendered suitable for re-use by subjecting it to fractional crystallisation, separating the precipitated ferrous sulphate and recovering mother liquor and adding to said liquor an amount of water substantially equal in volume to the amount of ferrous sulphate separated, thereby restoring an acid concentration once to twice normal in H_2SO_4 and one to three times normal in Cl ion. The limiter may be added in the form of a hydrochloric solution of peptonized gelatine, or of a tertiary heterocyclic base such as quinoline, naphthoquinoline, or a homologous hydrochloride.

[Second Edition.]

PATENT SPECIFICATION.

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Aug. 21, 1937:
Aug. 6, 1938:

Corresponding Applications in United Kingdom

No. 24581/38 } *dated Aug. 20, 1938.*
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517,998

(One Complete Specification left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1938.)

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COMPLETE SPECIFICATION

Improvements in or relating to Process of Pickling Iron and its Alloy.

I, PAUL DE LATTRE, a Belgian subject, of 73, rue de Bomerée, Mont s/Marchienne, Belgium, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to the cleaning of iron and its allows, particularly for preparing them for subsequent coating with another metal.

The usual method of cleaning consists in pickling the metal in a solution of hydrochloric acid. This method has the advantage of permitting the operation being carried out at a moderate temperature (for example, at from 20° C. to 40° C.) and of producing a salt (ferrous chloride) which is very soluble in cold water and has useful "mordant" properties. It has on the other hand the disadvantage of causing hardening of the metal by adsorption of hydrogen and of not lending itself to the regeneration of the residual solutions by simple and economical means.

To prevent the adsorption of hydrogen by the metal and the lowering of its mechanical properties resulting therefrom, it is known to add to the pickling bath products known as limiters or inhibitors which very appreciably reduce the action of the acid on the base metal whilst allowing it to act on the layer of oxides to be removed therefrom. Nevertheless these limiters which are mostly sulphonation extracts of heavy oil tars and which are simply added to the acid bath, have the drawback of reducing the speed of the removal of the layer of oxides and thus of retarding the cleaning of the base metal, even when the temperature of the pickling baths is raised up to 70° C. to 80° C.

Various processes have been proposed for regenerating the solution, but each of them suffers from some drawbacks.

It has in particular been proposed to eliminate the excess of ferrous chloride by saturating the residual liquid by a current of gaseous hydrochloric acid. The salt precipitates in the form of fine crystals ($Fe\ Cl_2 . 4\ H_2O$) which, after drying, may be treated with concentrated sulphuric acid. This process requires expensive plants, the running of which requires special knowledge.

It has also been proposed to treat the aqueous solutions of ferrous chloride directly with concentrated sulphuric acid in order to produce the equilibrium reaction :

$$H_2SO_4 + Fe\ Cl_2 \rightleftharpoons Fe\ SO_4 + 2\ H\ Cl.$$

If, starting from a residual solution rich in ferrous chloride and poor in hydrochloric acid, successive additions of sulphuric acid are made with a view to maintaining the concentration of free acid, the solution becomes rich in ferrous sulphate, gradually loses its chemical activity with respect to the oxides of iron, and gives rise to the formation on the pickled surfaces, as soon as these are withdrawn from the bath, of a white deposit of dehydrated sulphate which is difficultly soluble in water and is detrimental to the proper performance of the subsequent operations.

If starting from a cold saturated solution of ferrous chloride, sulphuric acid is added thereto keeping the solution at the ordinary temperature by strong cooling, there is obtained a mixture rich in hydrochloric acid and saturated in the cold with ferrous sulphate, the content of which is constant. The production of coatings of anhydrous sulphate is thus avoided but the proportion of free H Cl in the solution diminishes progressively in the course of the pickling and the operation slows up proportionately. Now this slowing down cannot be prevented by the addition of acid since the addition of sulphuric acid would give rise to an injurious excess of ferrous sulphate, whilst the addition of hydrochloric acid would cause an unallowable dilution of the bath, commercial hydrochloric acid only containing about a third of its weight of actual H Cl.

Furthermore in each of these cases the action of the limiters still further accentuates the reduction of the speed at which the oxides are dissolved.

The process according to my present invention is intended to obviate these various drawbacks. It is based on the observation that it is advantageous constantly to keep in the solution ferrous chloride formed by the action of hydrochloric acid on the ferrous sulphate, and that it is possible to utilise the presence of the ferrous chloride, which is much more soluble in water than the sulphate, to facilitate the precipitation of the latter in the cold.

To this end according to my invention I use as the pickling agent sulphuric acid with which I mix, with a limiter, hydrochloric acid in such proportions as to cause the formation of ferrous chloride at the expense of the ferrous sulphate produced by pickling, and I regenerate the bath by simultaneous additions of the two acids and of the limiter in such amount as to maintain substantially constant the concentrations of these three constituents and to keep up the partial conversion of ferrous sulphate into ferrous chloride. As this conversion takes place according to the reversible reaction :

$Fe\,SO_4 + 2\,HCl \rightleftharpoons Fe\,Cl_2 + H_2\,SO_4$

the respective proportions of the reagents will be determined in accordance with the law of Guldberg & Waage, so that the equilibrium of the reaction be displaced from left to right.

Preferably the initial bath consists of a mixture once to twice normal in H_2SO_4 and one to three times normal in Cl, with a limiter. To restore the concentration of free acid I may repeatedly add, in the course of the operation, suitable quantities of sulphuric acid and hydrochloric acid, each addition of hydrochloric acid being accompanied by an addition of the limiter. The latter preferably consists of peptonised gelatine or of a hydrochloride of a heterocyclic base.

When the ferrous sulphate concentration reaches the highest permissible amount, I eliminate the excess by fractional crystallisation and I obtain a solution saturated with ferrous sulphate, in which the four constituents, i.e. $Fe\,SO_4$, $Fe\,Cl_2$, H_2SO_4, $H\,Cl$, are in stable equilibrium at the temperature prevailing at the end of the crystallisation. This solution is brought back to its initial volume by adding thereto an amount of water corresponding substantially to the volume of eliminated ferrous sulphate thereby restoring an acid concentration once to twice normal in H_2SO_4 and one to three times normal in Cl ion, and it then forms the pickling bath which is constantly used over again and put into presence of iron, the required concentrations of H_2SO_4 and Cl being restored as the proportion of dissolved iron increases.

Under these conditions the enrichment of the solution in ferrous sulphate as a result of the pickling action necessarily keeps up the reaction as follows :

$Fe\,SO_4 + 2H\,Cl \longrightarrow Fe\,Cl_2 + H_2SO_4$

I further ascertained the surprising fact that the speed of pickling then is accelerated notwithstanding the presence of the aforesaid limiter, and this even at but slightly elevated temperatures, preferably of 50° C. to 55° C. The action of the ferrous chloride is doubly advantageous for not only does it prevent the presence of an excess of ferrous sulphate but it has a "mordant" effect that is favorable to the pickling. The bath can be used until it has an iron content considerably higher than that permissible with previous processes and the precipitation of the iron sulphate is easily effected by simply cooling the solution.

An example will enable the operation of the process according to my invention to be better understood.

To prepare the initial pickling bath when a spent solution is not available, I take an aqueous solution of sulphuric acid containing, for example, 98 grammes of H_2SO_4 per litre, to which I add hydrochloric acid in such proportion as to give a solution normal or twice normal in Cl.

To this mixture, which I heat to about 50° C., I add as a limiter a hydrochloric solution of peptonised gelatine, in the proportion of 12 Kg. of this solution per 100 Kg. of sulphuric acid at 60° Bé. in the bath.

To prepare this quantity of limiter 0.400 Kg. of ordinary gelatine is dissolved in 1.4 Kg. of water heated to 50° C. After the gelatine has dissolved there is added 0.2 Kg. of commercial hydrochloric acid of 20/22° Bé. This is heated to 80° C.—90° C. for ten minutes and the solution allowed to cool when it is poured into 10 Kg. of hydrochloric acid at 20° Bé. If sulphuric acid at 66° Bé is used for preparing the pickling bath the quantity of limiter will be raised from 12 to 15.4 Kg. per 100 Kg. of sulphuric acid in the bath.

When the maximum iron content in the bath is attained the residual solution is regenerated by fractional crystallisation of the iron sulphate in a manner known *per se*. The initial volume of the solution then is restored by an addition of water and the regenerated bath is again brought into presence of iron to be pickled.

Such bath ensures a very rapid pickling of the iron or iron alloy at the moderate

temperature of 50° C. to 55° C. without appreciably attacking the base metal.

Each time the pickling bath is enriched with sulphuric acid there is also added 12 to 15.4 Kg. of hydrochloric solution of gelatine per 100 Kg. of sulphuric acid added.

These successive additions of sulphuric acid and of hydrochloric acid containing the required quantity of peptonised gelatine are continued until the total iron content of the bath reaches the predetermined maximum, which may be 140 to 145 grammes per litre. I have found that this content is not detrimental to the coating, for example galvanising, of the pickled metal. A simple washing of the latter suffices to give to the layer of deposited metal all its qualities of evenness and brilliance. Each time the maximum iron content is reached, the solution is regenerated and used over again, as above described.

As stated above the gelatine may be replaced in the preparation of the limiter by a corresponding quantity of a hydrochloride of a tertiary heterocyclic base such as quinoline, naphthoquinoline or a homologous hydrochloride, dissolved in an excess of concentrated hydrochloric acid, or by any other suitable substance.

It is understood that the process according to the invention is not limited to the exact amounts nor to the precise method of operation of the above example.

Instead of preparing the initial bath as stated above, I may also prepare a suitable bath for example from a spent pickling bath consisting of an aqueous solution of sulphuric acid, twice normal for example, to which solution is added the quantity of hydrochloric acid (and limiter) required to form a solution once to three times normal in chlorine. Such a reagent, in which the concentrations in $H_2 SO_4$ and Cl ion are kept constant by suitable additions of both acids, and the iron concentration is increased by the pickling, leads after cooling to a mother liquor which, upon being separated from the iron sulphate and restored to its initial volume, permits of starting a new pickling cycle in the course of which the sequence of chemical reactions described above is reproduced.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is :—

1. A process of pickling iron and its alloys, using sulphuric acid and hydrochloric acid, characterised by pickling with production of ferrous sulphate by means of a sulphuric acid solution to which are added hydrochloric acid and a limiter, the proportions of the reagents being such as to cause the formation of ferrous chloride at the expense of the ferrous sulphate, and regenerating the solution by simultaneous additions of the two acids and of the limiter in such amounts as to maintain substantially constant the concentrations of these three constituents and to keep up the partial conversion of ferrous sulphate into ferrous chloride.

2. In a process according to claim 1, subjecting a used pickling solution to fractional crystallisation, separating the precipitated ferrous sulphate and recovering mother liquor, adding to said liquor an amount of water substantially equal in volume to the amount of ferrous sulphate separated thereby restoring an acid concentration once or twice normal in $H_2 SO_4$ and one to three times normal in Cl ion, and using over again said liquor as a pickling bath.

3. A process according to claim 1 or 2, characterised by adding the hydrochloric acid together with the limiter.

4. A process according to claim 3, characterised by the limiter being added in the form of a hydrochloric solution of peptonised gelatine.

5. A process according to any of the preceding claims, characterised by maintaining the temperature of the pickling solution at 50 to 55° C. during the pickling operation, notwithstanding the presence of the limiter.

6. A process according to any of the preceding claims, characterised by carrying on pickling with the same solution, with suitable additions of sulphuric acid, hydrochloric acid and limiter, until the total iron content of the solution reaches 140 to 145 gr. per litre, then separating ferrous sulphate by fractional crystallisation, restoring the initial volume of the solution, and resuming pickling with the restored solution.

7. A process of pickling iron and its alloys, substantially as hereinbefore described.

Dated this 20th day of August, 1938.

HASELTINE, LAKE & CO.,
28, Southampton Buildings,
London, England,
and
19—25, West 44th Street,
New York, U.S.A.,
Agents for the Applicant.

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